10.8. Methods for the determination of order

The order of a reaction can be determined by any of the following methods.

1. Integration method (Substitution in equation) :

This method involves using expressions relating the concentration and time for reactions of various orders, and fitting the appropriate expression to the experimental data (Table 10.1).

TABLE 10.1. Rate equations of various order.

Order	Differential form	Integrated form
0	$\frac{dx}{dt} = k$	$k = x/t$
1	$\frac{dx}{dt} = k\,(a-x)$	$k = \frac{1}{t}\ ln\ \frac{a}{a-x}$
2	$\frac{dx}{dt} = k\,(a-x)^2$	$k = \frac{1}{t}\ \frac{x}{a(a-x)}$
3	$\frac{dx}{dt} = k\,(a-x)^3$	$k = \frac{1}{2t}\ \frac{x\,(2a-x)}{a^2(a-x)^2}$

The expression which shows constancy of value of k indicates the appropriate order of the reactions. This is a method of hit and trial but was the first to be employed.

Example 10.9. *In the study of kinetics of decomposition of a reaction, the concentration of reactants were determined at different intervals. The following results were obtained.*

Time (*min.*)	0	20	40	100	125
Conc. (*mol litre*$^{-1}$)	0·1000	·0556	·0385	·0200	·0167

What is the order and rate constant for the reaction.

Solution. We substitute this data in the first order rate equation first and if this does not give a constant value of k, the same data is inserted in second order rate equation and so on.

Time	$a-x$	x	$k = \frac{2{\cdot}303}{t} \log \frac{a}{a-x}$	$k = \frac{1}{t} \times \frac{x}{a(a-x)}$
20	·0556	0·0444	= ·0342	= 0·399
40	·0385	0·0615	= ·0239	= 0·399
100	·0200	0·0800	= ·0161	= 0·400
125	·0167	0·0833	= ·0062	= 0·399

It is seen from the calculation that first order rate constant changes rapidly while the second order rate constant remains almost constant. Therefore, the reaction is second order and the rate constant is equal to = 0·400 mol^{-1} litre min^{-1}.

2. Graphical method.

The equation of rate constant for first order is

$$k = \frac{2{\cdot}303}{t} \log \frac{a}{(a-x)}$$

or

$$t = \frac{2{\cdot}303}{k} \log a - \frac{2{\cdot}303}{k} \log (a-x) \qquad \ldots(10.41)$$

There are only two variables in equation (10.41). If *log $(a-x)$ is plotted against t and a straight line is obtained* (Fig 10.3) the reaction is first order reaction.

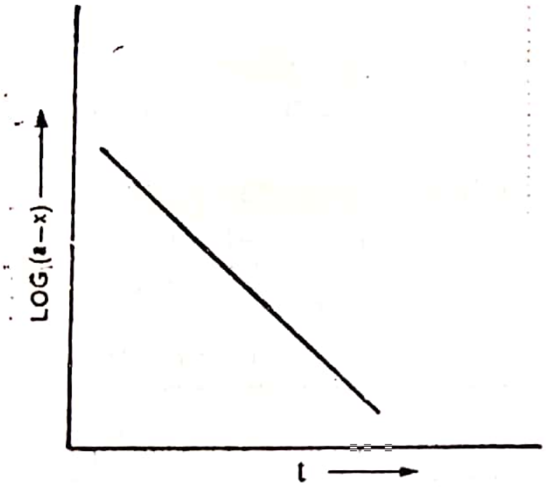

Fig. 10.3. Plot of log $(a-x)$ vs. time (t) in first order reaction.

$$\text{Slope} = -\frac{2{\cdot}303}{k} \qquad \ldots(10.42)$$

From the slope of the straight line, k can easily be determined.

The rate constant for the second order reaction is

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

or

$$t = \frac{1}{k\,(a-x)} - \frac{1}{ka} \qquad \ldots(10.43)$$

Since a is constant for a given experiment, it follows that by plotting $\frac{1}{(a-x)}$ *values against time t, a straight line is* obtained for second order reactions (Fig. 10.4). The slope of the line *i.e.* $\frac{1}{k}$ gives the value of rate constant of the reaction.

If the second order reaction contains two different reactants then

$$k = \frac{2{\cdot}303}{t\,(a-b)} \log \frac{(a-x)}{(b-x)} \cdot \frac{b}{a}$$

or

$$t = \frac{2{\cdot}303}{k\,(a-b)} \log \frac{(a-x)}{(b-x)} + \frac{2{\cdot}303}{k\,(a-b)} \log \frac{b}{a}$$

From eq. (10.26)

The plot of log $\frac{a-x}{(b-x)}$ vs. t is straight line (Fig. 10.5) and the slope is equal to $\frac{2\cdot303}{k\,(a-b)}$ which yields the value of k.

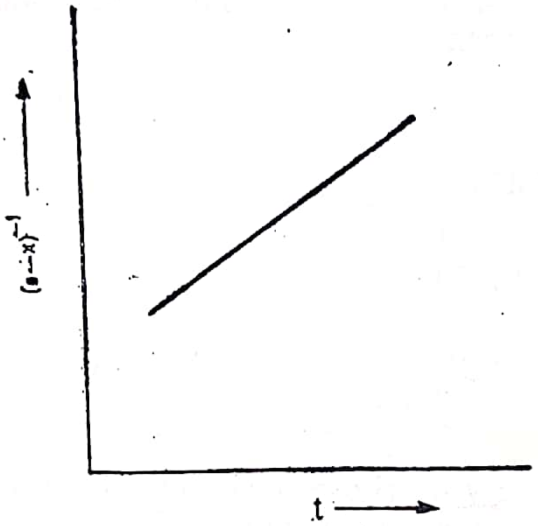

Fig. 10.4. Plot of $(a-x)^{-1}$ vs. time, t in second order reaction.

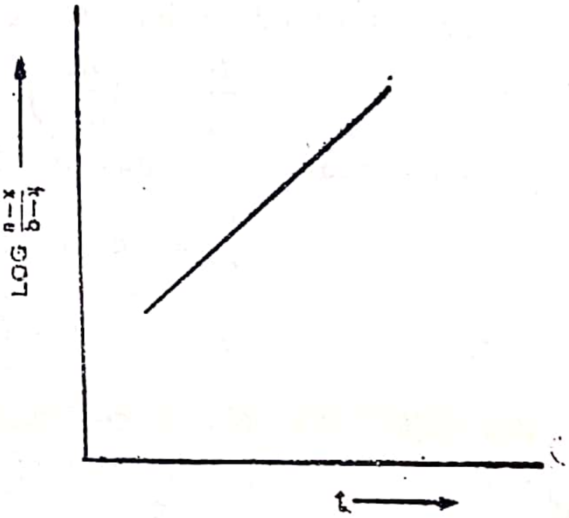

Fig. 10.5. Plot of log $\frac{(a-x)}{b-x}$ vs time, t in second order reaction in which the reactions have different concentrations a and b.

The rate constant of the third order reaction is given by

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \quad \text{from equation} \quad \ldots(10.33)$$

or

$$t = \frac{1}{2k}\,\frac{1}{(a-x)^2} - \frac{1}{2ka^2}$$

Plot of $(a-x)^{-2}$ vs. t yields a straight line (Fig. 10.6). The slope of the straight line is equal to $\frac{1}{2k}$. From this, k can be evaluated.

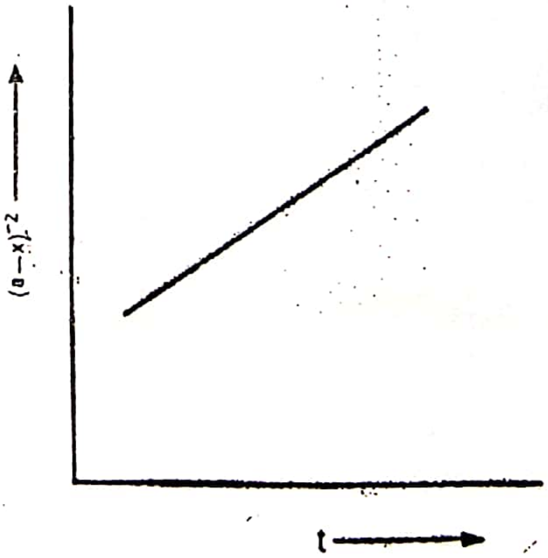

Fig. 10.6. Plot of $(a-x)^{-2}$ vs. t in third order reaction.

3. Method of equifractional parts (Half life method).

It has already been shown that

(*i*) t_f is independent of a : first order reaction

(*ii*) t_f is proportional to $\frac{1}{a}$: second order reaction

(*iii*) t_f is proportional to $\frac{1}{a^2}$: third order reaction

Thus is general

$$t_f \propto \left(\frac{1}{a}\right)^{n-1} \qquad \ldots(10.44)$$

where t_f is the time required to complete a definite fraction of the reaction and a is the initial concentration.

If in two different experiments the initial concentrations are a_1 and a_2 at the corresponding times t_1 and t_2 then

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad \ldots(10.45)$$

Taking logarithm of equation (10.45)

$$\log \frac{t_1}{t_2} = (n-1) \log \left(\frac{a_2}{a_1}\right)$$

$$\therefore \qquad n = 1 + \log \frac{t_1}{t_2} \Big/ \log \frac{a_2}{a_1} \qquad \ldots(10.46)$$

4. Ostwald's isolation method.

This method is applicable particularly in those reactions in which there are two or more reactants. The experiments are performed by taking all reactants except one in excess one by one. The reactant which is not taken in excess is called isolated. The order of reaction will be determined with respect to the isolated one. The order of the whole reaction will then be the total of these individual orders. For example in the reaction.

$$l\text{A} + m\text{B} + p\text{C} \longrightarrow \text{Products}$$

if the reactants B and C are in large excess, the order will be given by l, if C and A are in large excess the order will be m and similarly the order will be p if A and B are in large excess. The true order, n is given by

$$n = l + m + p$$

This method is known as **Ostwald's isolation method.**

5. Van't Hoff's differential method.

For the first order reaction

$$\frac{dx}{dt} = k\,(a-x)$$

For the second order reaction

$$\frac{dx}{dt} = k\,(a-x)^2 \text{ or } \frac{dx}{dt} = k(a-x)(b-x),$$

For third order reaction

$$\frac{dx}{dt} = k\,(a-x)^3$$

In general, $\frac{dx}{dt} = k\,(a-x)^n$ ...(10.47)

Putting $(a-x) = C$, the concentration at any instant

$$\frac{-dc}{dt} = kC^n \qquad \text{...(10.48)}$$

For two different initial concentrations C_1 and C_2 of reactants in two separate experiments

$$\frac{-dC_1}{dt} = kC_1^n \quad \text{and} \quad \frac{-dC_2}{dt} = kC_2^n$$

Taking logarithm,

$$log\left(\frac{-dC_1}{dt}\right) = log\ k + n\ log\ C_1 \qquad \text{...(10.49)}$$

$$log\left(\frac{-dC_2}{dt}\right) = log\ k + n\ log\ C_2 \qquad \text{...(10.50)}$$

The equation (10.49) and (10·50) give the relation

$$n = \frac{log\,(-dC_1/dt) - log\,(-dC_2/dt)}{log\ C_1 - log\ C_2} \qquad \text{...(10.51)}$$

The values of dC/dt can be obtained from the slopes of the C vs t plots. Substitution of these values for two different initial concentrations, n can be calculated.

Example 10.10. *At a certain temperature, the half life period for the decomposition of ammonia in contact with tungsten were as follows :*

Pressure (mm of Hg)	50	100	200
Half life period (Relative)	3·52	1·82	0·93

Find the order of the reaction.

Solution. First method.

Half life period, $t_{1/2}$ is independent of initial concentration, a for first order

For second order, $t_{1/2} \propto \frac{1}{a}$ or $t \times a = \text{constant}$

For third order, $t_1/_2 \propto \frac{1}{a^2}$ or $t \times a^2 = \text{constant}$

$t \times a$	$t \times a^2$
$3{\cdot}52 \times 50 = 176$	$3{\cdot}52 \times 50 \times 50 = 8800$
$100 \times 1{\cdot}82 = 182$	$1{\cdot}82 \times 100 \times 100 = 18200$
$200 \times 0{\cdot}93 = 186$	$0{\cdot}93 \times 200 \times 200 = 37200$

Since, $t \times a$ is almost constant, the reaction is second order reaction.

Second method. $n = 1 + \dfrac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$

$$\text{I} \qquad n = 1 + \frac{\log 3{\cdot}52 - \log 1{\cdot}82}{\log 100 - \log 50}$$

$$= 1{\cdot}95$$

$$\text{II} \qquad n = 1 + \frac{\log 1{\cdot}82 - \log 0.93}{\log 200 - \log 100}$$

$$= 1{\cdot}97$$

Thus, order of reaction is 2.

Example 10.11. *A substance 'A' is mixed with equal quanity of the substances B and C. At the end of 1000 seconds one half of the amount of A has reacted. What fraction will be left unreacted at the end of 2000 seconds, if the reaction is*

(*i*) *second order with respect to A.*

(*ii*) *zero order with respect to A.* (*Agra B.Sc. 1951*)